The effective and selective separation of (–)-epigallocatechin gallate by molecularly imprinted chitosan beads

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Abstract The (–)-epigallocatechin gallate (EGCG) imprinted chitosan beads (EICBs) were fabricated for the effective and selective separation of EGCG. The EGCG molecules interacted with the amino groups of chitosan in the imprinting process, resulting in a highly porous structure of EICBs and more adsorption sites. Consequently, EICBs exhibited better adsorption performance than non-imprinted chitosan beads. The maximum adsorption capacity of EGCG onto EICBs reached 135.50 mg/g at 313 K. The imprinting factor of EICBs was 4.22, indicating that EICBs possess good recognition ability and selectivity for EGCG. After five cycles of reuse, only a slight decrease (7.77%) in the adsorption capacity was observed, demonstrating the satisfactory reusability of EICBs. Furthermore, the adsorption of EGCG onto EICBs is deduced to be the monolayer adsorption on an energetically homogeneous surface; the hydrogen bonding between EGCG and EICBs is the main driving force for the adsorption. Our studies suggest that EICBs have a great potential for the effective and selective separation of EGCG.

Keywords (–)-Epigallocatechin gallate · Chitosan · Molecular imprinting technique · Adsorption

Introduction

Recently, green tea has become one of the popular drinks in the world due to its excellent therapeutic and protective effects on human health (Bansal et al. 2013; Reygaert 2014). Research indicates that green tea can reduce the risk of cancer, neurodegenerative, and cardiovascular diseases (Dube et al. 2010). These beneficial effects are attributed to tea polyphenols (TP) (López de Lacey et al. 2014), the major components of which are catechins. Catechins are comprised of (–)-epicatechin (EC), (–)-epicatechin gallate (ECG), (–)-epigallocatechin (EGC) and (–)-epigallocatechin gallate (EGCG) (Gadkari et al. 2015; Saklar et al. 2015). Among them, EGCG accounts for 50–80% of the total amount of catechins and possesses the most powerful biological activities such as antiviral, antitumor, antimicrobial activity, and neuroprotective effect (Min and Kwon 2014). Therefore, EGCG is widely used in the fields of foodstuff, beverage, and biomedicine (Dube et al. 2011; Liu et al. 2012). Furthermore, because of its versatile applications, the separation of EGCG from green tea attracted considerable attention in recent years (Wu et al. 2014).

Adsorption is an attractive approach for the separation of EGCG due to its advantages of high efficiency, simple operation process, easy reuse, and being eco-friendly (Gao et al. 2012; Wu et al. 2016). However, the EGCG extracted from green tea by the typical adsorption method is usually contaminated by other unfavorable components as a result of low selectivity, which reduces the beneficial effects of EGCG. Therefore, it is crucial to enhance the adsorption selectivity of EGCG for preserving these beneficial effects. The molecular imprinting technique is generally used to enhance the adsorption selectivity. A polymer processed by the molecular imprinting technique, regularly called the

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molecularly imprinted polymer (MIP), has specific cavities with affinity to template molecules (Song et al. 2012). Because of the high affinity and specificity to templates, MIP has been served in many fields such as separation, catalysis, and molecular sensors. Especially, several MIPs have been designed for the separation of EGCG. A molecularly imprinted silica gel was synthesized for the adsorption of EGCG (Zhang et al. 2013). The molecularly imprinted chitosan was also established for the separation of EGCG (Chen et al. 2012). In these studies, the adsorption selectivity of the adsorbents is adequately enhanced but the adsorption capacities are insufficient for further applications.

To enhance the adsorption capacity and selectivity, we developed a novel porous MIP from chitosan using EGCG as templates and polyethylene glycol (PEG) 4000 as porogen. Chitosan has the powerful adsorption capability toward various compounds such as proteins, dyes, and metal ions (Babel and Kurniawan 2003; Crini 2006). Moreover, chitosan has the advantages of biodegradable, biocompatible, and non-toxic (Tang et al. 2013). Therefore, chitosan is appropriate to be used as an adsorbent to separate bioactive materials for food and medicine due to its safety to human health (Sarbon et al. 2015). The resulting EGCG-imprinted chitosan beads (EICBs) were characterized using Fourier transform infrared (FTIR) spectroscopy and scanning electron microscopy (SEM). The adsorption kinetics and equilibrium of EGCG onto EICBs were investigated in detail; the adsorption selectivity and reusability of EICBs were evaluated.

Materials and methods

Materials

Chitosan with a molecular weight of 8×10^5 and a deacetylation degree of 85% was provided by Zhejiang Aoxing Biotechnology Co., Ltd., China. EGCG and TP were purchased from Hangzhou Yibei Jia Biotechnology Co., Ltd., China. Other chemicals with analytical grade were obtained from Tianjin Yingdaxigui Chemicals, China. Double distilled water was used for the preparation of solutions throughout the experiments.

Preparation of EICBs

Chitosan (0.5 g) was dissolved completely in 20 mL acetic acid–sodium acetate buffer (pH 5.0, 0.1 mol/L), followed by adding 10 μ L EGCG solution (5 g/L). The mixture was stirred at room temperature for 2 h to complete the imprinting process. Afterwards, 100 μ L PEG 4000 solution (10 g/L) was added into the mixture for the formation of

the porous structure. Then, the mixture was added dropwise into 50 mL NaOH solution (1 mol/L) using a syringe needle with an inner diameter of 0.3 mm. The drop was instantly gelled and formed beads when it was getting into contact with the NaOH solution. The resulting EICBs were retained in the NaOH solution for 2 h for the further solidification, followed by filtration and thorough rinsing with double distilled water. The EICBs were then cross-linked at 30 °C for 4 h with 20 mL ethylene glycol diglycidyl ether solution (1%, v/v) and rinsed completely with double distilled water. EGCG template molecules were removed with 10% (v/v) ethanol solution under ultrasonication. Finally, the EICBs were dried at -50 °C by vacuum-freeze-drying. Non-imprinted chitosan beads (NICBs) were fabricated using an identical method without the presence of EGCG. The average diameter of the swollen beads used in the adsorption was 2.1 mm.

Characterization of EICBs

FTIR spectrum was recorded on a KBr disk using a Tensor 27 Fourier transform infrared spectrometer (Bruker, Germany). The wavenumber ranged from 4000 to 500 cm^{-1} . The surface morphology of the beads was observed using a Nova NanoSEM 450 scanning electron microscope (FEI, USA).

Adsorption experiments

The EGCG stock was prepared by dissolving EGCG in double distilled water to the concentration of 500 mg/L and then diluted to an appropriate concentration in the adsorption experiments. The batch adsorption was conducted in a 250-mL flask with 100 mL EGCG solution and swollen beads (41.5 mg in dried weight). The flask was shaken at 120 rpm using a constant temperature shaker. The EGCG concentration in the solution was determined by measuring the absorbance at 270 nm using a UV-1100 ultraviolet–visible spectrophotometer (Mapada, China). The adsorption capacity was calculated by the following equation:

$$q_t = \frac{(C_0 - C_t)V}{m} \quad (1)$$

where q_t is the adsorption capacity at time t , mg/g; C_0 is the initial concentration of EGCG, mg/L; C_t is the concentration of EGCG at time t , mg/L; V is the solution volume, L; m is the dried weight of the beads, g.

Selectivity of EICBs

The TP was dissolved in double distilled water to the concentration of 100 mg/L. Then, EICBs or NICBs

(41.5 mg in dried weight) were added into 100 mL TP solution to perform the adsorption. After adsorption, the EGCG concentration in the solution was determined by an Agilent 1100 Series high performance liquid chromatography (Agilent technologies, USA) according to the previous work (Liu et al. 2012).

Reusability of EICBs

EGCG loaded beads were recovered with 20 mL ethanol solution (10%, v/v) under ultrasonication for 30 min, followed by thorough rinsing with double distilled water. The regenerated beads were used in the next adsorption process. Five adsorption–desorption cycles were carried out to evaluate the reusability of EICBs.

Results and discussion

Characterization of EICBs

FTIR spectrum is a reliable tool for determining the chemical structure of compounds. The FTIR spectra of CS, NICBs, and EICBs were measured to analyze the functional groups in the crosslinking reaction and the imprinting process. The synthesized NICBs and EICBs exhibited some alterations in the FTIR spectra compared with the original CS (Fig. 1). The overlapping band of N–H and O–H stretching vibration occurred at 3441 cm^{-1} in CS spectrum, but shifted to 3435 cm^{-1} in NICBs spectrum and 3431 cm^{-1} in EICBs spectrum. The band of C–O stretching vibration in $\text{C}_3\text{--OH}$ of CS appeared at 1088 cm^{-1} , which shifted to lower frequency at 1076 and 1074 cm^{-1} for NICBs and EICBs, respectively. These alterations suggest that the hydroxyl and amino groups of chitosan associated with the crosslinking reaction. Moreover, the band of --NH_2 groups appeared at 1597 cm^{-1} in CS spectrum. It weakened in the NICBs spectrum but had no

Fig. 1 FTIR spectra of CS, NICBs, and EICBs

evident changes in the EICBs spectrum. This result reveals that the imprinting process prevented the amino groups of chitosan from the crosslinking. The amino groups of chitosan are main active sites in adsorption (Crini 2006). Thereby, more adsorption sites are remained in EICBs compared with NICBs, which will facilitate the adsorption performance of EICBs.

The morphology of NICBs and EICBs was examined by SEM. As shown in Fig. 2, both NICBs and EICBs exhibited the porous structure, and the pore size of EICBs was much greater than that of NICBs. The porous structure of the beads was formed due to the phase inversion process according to the previous work (Zhao et al. 2007) and the addition of PEG 4000 (Kim and Lee 1998). When the chitosan solution was dripped into the NaOH solution, NaOH reacted with both the protonated amino groups of chitosan and the solvent, acetic acid. Therefore, the chitosan drop was gelled to form a porous sphere. For EICBs, most of the amino groups of chitosan interacted with the EGCG molecules in the imprinting process, which reduced the reaction sites of chitosan molecules with NaOH in the phase inversion and resulted in a flexible network of the

Fig. 2 Scanning electron microscope graphs of NICBs (a) and EICBs (b)

matrix. Accordingly, a larger pore size was obtained for EICBs relative to NICBs. The highly porous structure of EICBs will reduce the resistance of mass transfer and enhance the adsorption performance.

Adsorption kinetics

The adsorption kinetics of EGCG onto NICBs and EICBs was investigated to understand the adsorption behavior. The adsorption experiments were carried out at 303 K, and the initial concentration of EGCG was 60 mg/L. The adsorption capacity of EGCG onto EICBs dramatically increased in the initial 10 min, and gradually approached equilibrium within 50 min (Fig. 3a). The rapid increase in adsorption capacity during the initial stage is due to the sufficient adsorption sites available on the beads and the high EGCG concentration in the solution. With the time extending, the adsorption sites were gradually occupied by EGCG molecules, and the adsorption process progressed from the surface to the interior of the beads. These changes resulted in the slowdown in the adsorption rate and the final adsorption equilibrium. Compared with EICBs, NICBs exhibited a similar adsorption behavior. However, longer equilibrium time (180 min) was required for NICBs relative to EICBs, which indicates that the highly porous structure of EICBs facilitates the adsorption rate.

To understand the adsorption mechanism, the adsorption kinetic data were first analyzed using the pseudo-first-order kinetic model. The linear form of the pseudo-first-order kinetic equation is given as Eq. (2) (Ho 2006).

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (2)$$

where q_e and q_t are the adsorption capacities at equilibrium and at time t , respectively, mg/g; k_1 is the rate constant of the pseudo-first-order kinetic model, min^{-1} .

The fitting plots of $\ln(q_e - q_t)$ versus t were obtained from the kinetic data, and the kinetic parameters q_e and k_1 were calculated from the intercepts and slopes of the plots, respectively. However, the correlation coefficients (R^2)

were only 0.928 and 0.929 for NICBs and EICBs, respectively (Table 1). Especially, the calculated $q_{e,\text{cal}}$ values (90.71 mg/g for NICBs and 65.84 mg/g for EICBs) were inconsistent with the experimental $q_{e,\text{exp}}$ values (109.82 mg/g for NICBs and 125.62 mg/g for EICBs). These results suggest that the pseudo-first-order kinetic model was not appropriate to describe the adsorption of EGCG. Therefore, the adsorption kinetic data were further analyzed by the pseudo-second-order kinetic model to clarify the adsorption mechanism. The linear form of the pseudo-second-order kinetic equations is expressed as Eq. (3) (Ho 2006).

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (3)$$

where k_2 is the rate constant of pseudo-second-order model, g/(mg min).

The fitting plots for the pseudo-second-order kinetic model are presented in Fig. 3b. It can be clearly observed that the pseudo-second-order kinetic plots were very close to the experimental data, which indicates that the adsorption of EGCG well followed the pseudo-second-order kinetic model. This deduction was further validated by the high R^2 values (0.997 for NICBs and 1.000 for EICBs) and the consistency of the $q_{e,\text{cal}}$ values (116.14 mg/g for NICBs and 130.38 mg/g for EICBs) with the $q_{e,\text{exp}}$ values (Table 1). The pseudo-second-order kinetic model is usually used to describe an adsorption process through sharing or exchange of electrons (Ho 2006). The EGCG molecule has several hydroxyl groups, while EICBs and NICBs possess abundant amino groups. Thus, the hydrogen bonds can be formed between EGCG and EICBs/NICBs, which is likely the adsorption mechanism of EGCG.

The adsorption process of the porous absorbent usually has multiple steps, including the bulk diffusion, film diffusion, intraparticle diffusion and finally adsorption on the active sites. Accordingly, the adsorption kinetic data were also analyzed using the intraparticle diffusion model expressed as Eq. (4) (Singh et al. 2012).

Fig. 3 Adsorption kinetics (a), pseudo-second-order kinetic plots (b) and intraparticle diffusion plots (c) for the adsorption of EGCG onto NICBs and EICBs

Table 1 Kinetic parameters for the adsorption of EGCG onto NICBs and EICBs

Beads	$q_{e,exp}$ (mg/g)	Pseudo-first-order			Pseudo-second-order			Intraparticle diffusion	
		$q_{e,cal}$ (mg/g)	k_1 (min ⁻¹)	R^2	$q_{e,cal}$ (mg/g)	k_2 (g/(mg min))	R^2	k_i (mg/(g min ^{1/2}))	R^2
NICBs	109.82	90.71	0.0289	0.928	116.14	0.664×10^{-3}	0.997	5.160	0.987
EICBs	125.62	65.84	0.0312	0.929	130.38	1.144×10^{-3}	1.000	11.006	0.988

Table 2 Langmuir and Freundlich constants for the adsorption of EGCG onto NICBs and EICBs

Beads	T (K)	Langmuir constants			Freundlich constants		
		b (L/mg)	q_m (mg/g)	R^2	K_F (mg/g)	n	R^2
NICBs	303	0.524	115.87	0.998	49.74	3.917	0.761
	313	0.536	117.37	0.998	47.38	3.472	0.793
	323	0.615	112.61	0.998	49.96	3.920	0.672
EICBs	303	0.549	134.05	0.998	54.25	3.415	0.777
	313	0.577	135.50	0.998	55.06	3.380	0.802
	323	0.662	131.93	0.998	56.70	3.559	0.748

$$q_t = k_i \cdot t^{1/2} + C_i \quad (4)$$

where k_i is the intraparticle diffusion rate constant, mg/(g min^{1/2}); C_i is the constant that is proportional to the thickness of the boundary layer, mg/g.

The plots of q_t versus $t^{1/2}$ are shown in Fig. 3c. The multi-linearity of the fitting plots, including two slopes and one plateau, was observed for both EICBs and NICBs. The first linear portion with a steep slope is assigned to the film diffusion. The second linear portion represents the intraparticle diffusion. The third portion is attributed to the adsorption equilibrium. The intraparticle diffusion is usually the rate-limiting step in a well-stirred system. Therefore, the k_i values were calculated from the slopes of the second linear portion, and the results are presented in Table 1. A higher k_i value was obtained for EICBs (11.006 mg/(g min^{1/2})) relative to NICBs (5.160 mg/(g min^{1/2})), which illustrates that EICBs had better intraparticle diffusion than NICBs. This result agreed with the adsorption equilibrium time mentioned above and reflected the highly porous structure of EICBs.

Adsorption isotherm

The adsorption isotherm is the fundamental basis for investigating the interaction behavior between adsorbents and adsorbates (Nghah and Fatinathan 2010). Herein, a serial of adsorption equilibrium experiments were conducted at 303, 313, and 323 K in the EGCG initial concentrations of 20, 31.7, 40, 50, 66, and 81.5 mg/L. The Langmuir and Freundlich isotherms were used to analyze the adsorption equilibrium data. The linear forms of the

Langmuir and Freundlich isotherms are expressed as Eqs. (5) and (6), respectively (Chen et al. 2011).

$$\frac{C_e}{q_e} = \frac{1}{b \cdot q_m} + \frac{C_e}{q_m} \quad (5)$$

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (6)$$

where C_e is the equilibrium concentration of EGCG, mg/L; q_m is the theoretical maximum adsorption capacity, mg/g; q_e is the equilibrium adsorption capacity, mg/g; b is the Langmuir adsorption constant, L/mg; K_F is the Freundlich isotherm constant, mg/g; n is the heterogeneity factor.

Based on the correlation coefficients R^2 in Table 2, the Langmuir isotherm model was making more sense to describe the EGCG adsorption onto NICBs and EICBs than the Freundlich model. The Langmuir model usually describes the monolayer adsorption on an energetically homogeneous surface, whereas Freundlich model describes the multilayer adsorption on an energetically heterogeneous surface (Wu et al. 2014). Therefore, it is assumed that the adsorption of EGCG onto NICBs and EICBs is the monolayer adsorption on an energetically homogeneous surface. Similar adsorption mechanism of other adsorbates onto chitosan beads was addressed in the previous literatures (Jiang et al. 2012; Zuo 2014). The Langmuir adsorption constant b reflects the affinity of the adsorbent for the adsorbate. At a certain temperature, the b value of EICBs was greater than that of NICBs, demonstrating that EICBs had a better affinity for EGCG than NICBs. Furthermore, the maximum adsorption capacity (q_m) of EICBs obtained from the Langmuir isotherm reached 135.50 mg/g at 313 K. This value was higher than the q_m values of NICBs and other biosorbents in the previous reports (Chen

et al. 2012; Wu et al. 2015). As discussed above, the imprinting process prevented the amino groups of chitosan from the crosslinking, which resulted in a lower crosslinking degree and more flexible structure in EICBs. The flexible structure provided the access facilitation for EGCG. Therefore, EICBs exhibited better affinity and adsorption capacity for EGCG than NICBs.

A dimensionless factor R_L , reflecting the essential characteristic of the Langmuir isotherm, can be calculated from the Langmuir constant b .

$$R_L = \frac{1}{1 + b \cdot C_0} \quad (7)$$

where C_0 is the initial EGCG concentration, mg/L.

The R_L value categorizes the adsorption as unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$) (Suc and Ly 2013). Herein, the calculated R_L values for the EGCG adsorption were <1 and >0 , suggesting that the EGCG adsorption process is favorable.

Adsorption thermodynamics

Thermodynamics parameters can be calculated from the Langmuir equilibrium constant (K_L) according to the following equations:

$$\Delta G^\circ = -RT \ln K_L \quad (8)$$

$$\ln K_L = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (9)$$

where ΔG° is the standard Gibbs free energy change, kJ/mol; ΔH° is the standard enthalpy change, kJ/mol; ΔS° is standard entropy change, J/(mol K); T is the temperature, K; R is the gas constant, 8.314 J/(mol K); K_L is the Langmuir equilibrium constant with the unit of liter per mole (Liu 2009), which can be obtained by multiplying the Langmuir constant b with the molar weight of EGCG according to the previous study (Yan et al. 2011).

By plotting $\ln K_L$ versus $1/T$, the ΔH° and ΔS° values were calculated from the slopes and intercepts of the linear fitting plots, respectively. Table 3 presents the calculated thermodynamic parameters of the EGCG adsorption onto NICBs and EICBs. The negative ΔG° values illustrate the spontaneous nature of EGCG adsorption. ΔG° decreased with increasing the temperature, indicating that the EGCG adsorption is more favorable at higher temperature. The ΔH° values were positive for the EGCG adsorption, which reveals the endothermic nature of this adsorption. In general, the enthalpy change is corresponding to the interactions involved in the adsorption. The magnitude of ΔH° values for van der Waals interactions, hydrogen bonding, and chemisorption lies in the range of 4.2–8.2, 2–40, and 62.8–83.7 kJ/mol, respectively (Oopen et al. 1991). In this

Table 3 Thermodynamic parameters for the adsorption of EGCG onto NICBs and EICBs

Beads	T (K)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/(mol·K))
NICBs	303	−31.21	6.43	124.07
	313	−32.30		
	323	−33.70		
EICBs	303	−31.33	7.61	128.37
	313	−32.49		
	323	−33.90		

study, the ΔH° values for NICBs and EICBs were 6.43 and 7.61 kJ/mol, respectively. The van der Waals interactions usually occur in the physical adsorption, whereas the adsorption of EGCG does not follow the physical adsorption based on the kinetic and isotherm analyses mentioned above. Therefore, our results indicate that the hydrogen bonding between EGCG and EICBs/NICBs is the main driving force for the adsorption. In addition, and the positive ΔS° values imply the increase in the randomness at the interface of the beads and solution during the adsorption.

Selectivity of EICBs

The adsorption selectivity of EICBs was evaluated by measuring the EGCG concentration in TP before and after adsorption. The adsorption selectivity of the imprinted polymer toward the template molecule is usually determined by the imprinting factor (IF). The IF of EICBs was calculated using the following equations (Nantasenamat et al. 2007; Yang et al. 2013).

$$k' = \frac{C_{ad}}{C_e} \quad (10)$$

$$IF = \frac{k'_{EICBs}}{k'_{NICBs}} \quad (11)$$

where k' is the retention factor; C_{ad} is the EGCG concentration adsorbed at equilibrium, mg/L; k'_{EICBs} and k'_{NICBs} are the retention factors of EICBs and NICBs, respectively.

There is a positive correlation of IF value with the adsorption performance. The higher the IF value is, the higher the adsorption selectivity is (Wu et al. 2003). The calculated IF for EICBs was 4.22, which demonstrates the good template recognition ability and adsorption selectivity of EICBs. Moreover, this value is relatively higher than that in the previous report (Chen et al. 2012). Because of the molecular imprinting, the specific cavities created in the MIP were in accordance with the template molecular in size, shape and coordination geometry (Liu et al. 2011). Therefore, EICBs exhibited excellent selectivity for EGCG.

Reusability of EICBs

The reusability of the adsorbent is an important factor influencing the process economics. Thereby, five cycles of adsorption–desorption were conducted to evaluate the reusability of EICBs. Because some adsorption sites were damaged in the consecutive adsorption–desorption, the adsorption capacity of EICBs decreased gradually from 124.31 to 114.65 mg/g with increasing the reuse cycles. After five cycles of reuse, only a slight decrease (7.77%) in the adsorption capacity was observed, which indicates that EICBs have a satisfactory reusability and stability for the EGCG adsorption. The NICBs showed a similar pattern of reusability, with 10.17% decrease in the adsorption capacity after five cycles of reuse.

Conclusion

The EICBs were fabricated from chitosan using EGCG as template molecules for the effective and selective adsorption of EGCG. The EGCG molecules interacted with the amino groups of chitosan in the imprinting process, which resulted in a highly porous structure of EICBs and more adsorption sites. Consequently, EICBs exhibited a better adsorption performance than NICBs. The maximum adsorption capacity of EGCG onto EICBs obtained from the Langmuir isotherm reached 135.50 mg/g at 313 K. The imprinting factor of EICBs was 4.22, confirming the good recognition ability and selectivity of EICBs for EGCG molecules. After five cycles of reuse, only a slight decrease (7.77%) in the adsorption capacity was observed, suggesting the satisfactory reusability of EICBs. Furthermore, the adsorption of EGCG onto EICBs is determined to be the monolayer adsorption on an energetically homogeneous surface; the hydrogen bonding between EGCG and EICBs may be the main driving force for the adsorption. Our studies suggest that EICBs have a great potential for the effective and selective separation of EGCG.

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